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Solid State Structure and Crystallization of Strongly-Interacting Polymer Mixtures: Poly(ethylene oxide) and Styrene-Hydroxystyrene Random Copolymer Fractions

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Beamline(s): X27C

Time-resolved synchrotron wide- and small-angle X-ray scattering experiments were performed at beamline X27C at NSLS, BNL to investigate the crystallization behavior and microstructure development of poly(ethylene oxide) fractions and selected melt-miscible blends. The isothermal crystallization behavior of a PEO fraction with $M_w = 53,500$ can be fitted to a single Avrami expression. The initial decrease of average SAXS long periods is ~ 2 -3 nm, similar to that of polydisperse PEO.¹ Two fractionated styrene-hydroxystyrene copolymers [LMW-SHS: $M_w = 31,700$ and HWM-SHS: $M_w = 72,700$] were blended with the 53.5K PEO fraction. Avrami plots of PEO/SHS blends exhibit at least two crystallization processes as shown in Figure 1. For blends containing 20% SHS, the initial decrease of average SAXS long period is ~ 5 -10 nm (see Figure 2). It is observed that HMW-SHS blends crystallized significantly faster than LMW-SHS blends due to the larger impurity length scale of the low molecular weight SHS fraction. It is also observed that the end of the very high apparent n region in Avrami plots is close to the time when SAXS long period and crystalline thickness become constant.

This data strongly suggest the following model for crystallization of the SHS blends, and likely for other melt-miscible blends as well. Early in the process, crystallization occurs via growth of relatively widely-spaced lamellae organized into a branched sheaf-like structure. Booth and Hay estimated that n could be as high as 14 for such a highly branched structure.² As crystallization proceeds, growth of subsidiary lamellae in uncrystallized regions between lamella occurs, leading to a reduction in mean L and l_c , as observed experimentally. At longer times, infilling reduces L and l_c to constant values and crystallization is completed close to the superstructure boundary. This leads to a return to 'normal' Avrami exponents.

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References: 1. M. S. Lisowski, Q. Liu, J. Cho, J. Runt, Y. Yeh, B. S. Hsiao, "Crystallization behavior of Poly(ethylene oxide) and its Blends using Time-Resolved Wide- and Small-Angle X-ray Scattering," *Macromolecules* **33**, 4842, 2000.
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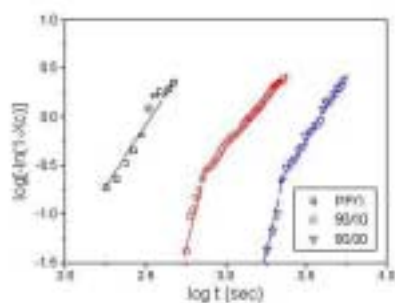


Figure 1. Avrami plots of PEO and LMW-SHS/PEO blends at $T_c = 48^\circ\text{C}$.

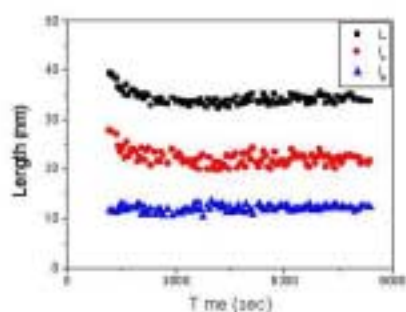


Figure 2. Development of SAXS microstructure parameters of LMW-SHS 20 wt % blend at $T_c = 48^\circ\text{C}$.